EQUILIBRIUM, ISOTHERM AND KINETIC STUDIES OF FLUORIDE ADSORPTION ON ACTIVATED RICE HUSK ASH

MICHAEL EMMANUEL¹, DANBATURE WILSON LAMAYI, ZACCHEUS SHEHU, PIPDOK SOLOMON KWARSON
Department of Chemistry, Gombe State University, PMB 127, Gombe, Gombe State, Nigeria
Email: mikolalaem143@gmail.com

Received 2018.1.25-Accepted 2018.1.128

ABSTRACT
Water pollution is a major problem to health and development of humans. The thermodynamic and kinetic parameters of activated rice husk ash (ARHA) for the defluoridation of water were carried out using Langmuir and Freundlich adsorption Isotherms. Results showed that activated rice husk ash is very effective in the defluoridation of water with about 86.1 % fluoride removal at a reaction time of 60 minutes. The values of ΔGads were found to be below -20 kJ mol⁻¹, which is consistent with physisorption mechanism of adsorption. Fluoride adsorption on ARHA was found to be endothermic from the positive values of enthalpy of adsorption ΔHads. Also, ASads was found to be positive, indicative of a spontaneous adsorption process of the fluoride

Key word: Activated Rice Husk Ash, Adsorption, Fluoride, Isotherm, Kinetics

INTRODUCTION
Pollution is a major problem around the world. There exist two major types of pollution; air and water pollution, other types of pollution such as soil, noise, light pollution and many more [1]; this paper discussed more of water pollution. Water pollution is said to be any change or modification in the physical, chemical and biological properties of water bodies (e.g. lakes, rivers, aquifers and groundwater) that has detrimental consequences on living things. Drinking water has for long, been contaminated with some dangerous chemical compounds such as arsenic, lead, fluoride etc. Dental and skeletal fluorosis is caused by the consumption of water containing fluoride ions above the WHO acceptable dosage (1.0 – 1.5mg/L) [2].

There are different methods available for the removal of fluoride in drinking water. These methods include; coagulation, precipitation [3, 4], reverse Osmosis [5], ion exchange, and removal by adsorption with adsorbent [6]. Of all these techniques, the method of adsorption was found and reported to be the most effective and cheapest way of defluoridation.

There are certain benefits and demerits of fluoride in drinking water. Although, fluoride in small quantity is an essential composition of bones and for the formation of teeth enamel in animals and humans, [7] high amount causes irreversible demineralization of bones and tooth tissues, also known as dental and skeletal fluorosis or mottled teeth [8,9]. Due to the high silica content of rice husk ash, it is found to be a good adsorbent for the removal of fluoride from water [10]. The techniques employed in the production of the ash, determines the type of ash to be produced.

MATERIALS AND METHODS
Preparation of Rice Husk Ash
The rice husk ash was prepared according to the method described by Danbature, et.al. [11].

Batch adsorption studies
Analysis for the removal of fluoride was carried out using a UV Spectrophotometer. (Model JENWAY 6300) [11]. Five different flasks labelled E1, E2, E3, E4 and E5 corresponding to the weight of the adsorbent of 0.5, 1.0, 1.5, 2.0 and 2.5g respectively. In each of the determination of fluoride removal using various adsorbents, various effects such as adsorbent dose, contact time, temperature and pH were determined, using (30 °C to 60 °C) for temperature, (0.5 to 2.5g) for adsorbent dosage, (10 to 60 min) for contact time and (2 to 12) for pH. pH adjustment was done using 1.0 M H₂SO₄ and 1.0 M NaOH.

Fluoride Ion Analysis
The percentage removal of fluoride ion and amount adsorbed (mg/g) were calculated using the following equations;

\[
\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100
\]

\[
\text{Amount adsorbed (q_e)} = \frac{(C_i - C_e)}{m} \times V
\]

Where; Cᵢ is the initial concentration of the fluoride solution (mg/L), Cₑ is the equilibrium concentration of the fluoride solution (mg/L), M is the mass of the adsorbent (g), and V is the volume of the fluoride test solution (L).

Adsorption Studies
To successfully carry out the analysis of the adsorption process, isotherm is an important tool. The experimental data were analyzed with Langmuir and Freundlich as the two most commonly use isotherms models.

Langmuir adsorption isotherm was used for the study of the adsorption process and assumes that adsorption takes place on a homogeneous surface of the adsorbent [12]. The linearized equation is given by equation (3).

\[
\frac{C_e}{q_e} = \frac{1}{q_m A F K_I} + \frac{C_e}{q_m A F}
\]

Where, Cₑ is the equilibrium concentration of the fluoride solution (mg/L) remaining, qₑ is the amount of fluoride adsorbed; qₑmax and Kₑ are the Langmuir isotherm constants

Freundlich adsorption isotherm considers the multilayer adsorption and depends on the assumption that a multiple layer adsorption is also possible on a heterogeneous surface [12]. The linearized equation is given in equation (4).

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where, Kₑ is an indication of the adsorption capacity of the adsorbent, the higher the value of Kₑ, The Higher The adsorption capacity; 1/n is a
measure of the intensity of adsorption. Values of 1/n are always less than 1. The closer the value of 1/n is to one, the more the adsorption process is favoured [13].

Kinetic Studies

Pseudo first-order and pseudo second-order kinetic models were used to determine the kinetics of adsorption of fluoride on the ARHA surface. Correlation co-efficient (R²) was used to determine which of the model best describes the kinetics of the adsorption of fluoride on ARHA. Values of R² close or equal to 1, indicates that there is high degree of accuracy of the values to the model used. Adsorption kinetic studies describe the amount of solute taken up by the ARHA with respect to time of exposure. [14]

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad 5
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad 6
\]

k₁ is the first order rate constant with the unit of inverse time, qₑ and qₑ are the adsorption capacity of the adsorbent at equilibrium and at time t, respectively. Equation 5 and 6 are the pseudo – first order and pseudo – second order kinetic models used respectively.

RESULTS AND DISCUSSION

Effect of adsorbent

The effect of the dosage of adsorbent on the adsorption of fluoride with initial concentration of 5mg/L was studied and the results shown in figure 1. It can be seen that the percentage of removal increased with increasing dosage of adsorbent. The largest percentage removal was 79.1% exhibited at 2.5 g; in table 1, it can be seen that the adsorption loading of fluoride decreases with increasing dosage of adsorbent. The influence of dosage of adsorbent is mainly related to its surface area [15].

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Ci (mg/L)</th>
<th>Ce (mg/L)</th>
<th>Ci - Ce (mg/L)</th>
<th>% Removal</th>
<th>qₑ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E₁ = 0.5</td>
<td>5</td>
<td>2.172</td>
<td>2.783</td>
<td>55.7</td>
<td>139.15</td>
</tr>
<tr>
<td>E₂ = 1.0</td>
<td>5</td>
<td>1.869</td>
<td>3.131</td>
<td>62.6</td>
<td>78.275</td>
</tr>
<tr>
<td>E₃ = 1.5</td>
<td>5</td>
<td>1.696</td>
<td>3.304</td>
<td>66.1</td>
<td>55.067</td>
</tr>
<tr>
<td>E₄ = 2.0</td>
<td>5</td>
<td>1.347</td>
<td>3.653</td>
<td>73.1</td>
<td>45.663</td>
</tr>
<tr>
<td>E₅ = 2.5</td>
<td>5</td>
<td>1.043</td>
<td>3.957</td>
<td>79.1</td>
<td>39.57</td>
</tr>
</tbody>
</table>


Table 1: Effect of adsorbent dose

Effect of pH

The effect of pH on the adsorption of fluoride by (ARHA) is shown in table 2 and figure 2. The results showed that adsorption was maximum at pH of 2.0 and removal was not favoured at pH above 2.0. This can be attributed to the distribution of fluoride as HF which is controlled by pH of aqueous solution [12]. As can be calculated from equation 1 [16], fluoride ion is dominated species when pH of the solution is higher than pKa (3.16) of HF [12]. It is also seen in table 2 when pH of the solution exceeded 2.0; there is steady decrease of adsorption. This may be explained by considering the pHₑ. The surface charge of the ARHA is assessed by the zero point charge (pHₑ= 6.0). At pH < pHₑ, the surface charge is positive, at pH = pHₑ, the surface is neutral and at pH > pHₑ, the surface charge is negative. As fluoride is negatively charge, so it preferentially attacks the adsorbents surface when the surface is positive in charge. At a pH below pHₑ, more of the surface sites are positively charged and fluoride ion will be adsorbed to a greater extent due to the attractive force between fluoride ions and positive charge of the rice husk ash. At pH 2.0, the specific adsorption of fluoride on (ARHA) is due to the electrostatic interaction between positively charged adsorbent surface and negatively charged fluoride ions. [12, 17].


Table 2: Effect of pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Absorbent (g)</th>
<th>Time (min)</th>
<th>Ci (mg/L)</th>
<th>Ce (mg/L)</th>
<th>Ci - Ce (mg/L)</th>
<th>% Removal</th>
<th>qₑ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.5</td>
<td>5</td>
<td>1.696</td>
<td>3.304</td>
<td>2.608</td>
<td>73.1</td>
<td>45.663</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>5</td>
<td>2.217</td>
<td>2.783</td>
<td>0.566</td>
<td>55.7</td>
<td>27.83</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>5</td>
<td>2.391</td>
<td>2.609</td>
<td>0.228</td>
<td>55.7</td>
<td>27.83</td>
</tr>
<tr>
<td>10</td>
<td>2.5</td>
<td>5</td>
<td>2.478</td>
<td>2.522</td>
<td>0.056</td>
<td>55.7</td>
<td>27.83</td>
</tr>
<tr>
<td>12</td>
<td>2.5</td>
<td>5</td>
<td>2.565</td>
<td>2.435</td>
<td>0.124</td>
<td>48.7</td>
<td>24.35</td>
</tr>
</tbody>
</table>

Fig. 1: Percentage fluoride removal versus adsorbent dose

Effect of contact time

The removal of fluoride as a function of contact time is shown in fig 3. It was observed that with fixed amount of adsorbent defluoridation increases with increase in time of exposure and then equilibrium is reached after 50 minutes, as in fig 3.
Fig. 3: Effect of contact time

Table 3: Effect of contact time

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbent (g)</th>
<th>C&lt;sub&gt;i&lt;/sub&gt; (mg/L)</th>
<th>C&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
<th>C&lt;sub&gt;i&lt;/sub&gt; - C&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
<th>% Removal</th>
<th>q&lt;sub&gt;t&lt;/sub&gt; (mg/L)</th>
<th>Log q&lt;sub&gt;e&lt;/sub&gt;</th>
<th>Log C&lt;sub&gt;e&lt;/sub&gt;</th>
<th>C&lt;sub&gt;e&lt;/sub&gt;/q&lt;sub&gt;e&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.5</td>
<td>5</td>
<td>2.217</td>
<td>2.783</td>
<td>55.7</td>
<td>27.83</td>
<td>1.445</td>
<td>0.346</td>
<td>0.079</td>
</tr>
<tr>
<td>20</td>
<td>2.5</td>
<td>5</td>
<td>1.826</td>
<td>3.174</td>
<td>63.5</td>
<td>31.74</td>
<td>1.502</td>
<td>0.262</td>
<td>0.058</td>
</tr>
<tr>
<td>30</td>
<td>2.5</td>
<td>5</td>
<td>1.347</td>
<td>3.653</td>
<td>73.1</td>
<td>36.53</td>
<td>1.563</td>
<td>0.129</td>
<td>0.037</td>
</tr>
<tr>
<td>40</td>
<td>2.5</td>
<td>5</td>
<td>1.043</td>
<td>3.957</td>
<td>79.1</td>
<td>39.57</td>
<td>1.597</td>
<td>0.018</td>
<td>0.026</td>
</tr>
<tr>
<td>50</td>
<td>2.5</td>
<td>5</td>
<td>0.696</td>
<td>4.364</td>
<td>86.1</td>
<td>43.64</td>
<td>1.639</td>
<td>-0.157</td>
<td>0.016</td>
</tr>
<tr>
<td>60</td>
<td>2.5</td>
<td>5</td>
<td>0.696</td>
<td>4.364</td>
<td>86.1</td>
<td>43.64</td>
<td>1.639</td>
<td>-0.157</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Effect of Temperature

The effect of temperature was studied using the method reported by Amrani and Tazrouti [18] and the result is as shown figure 4. The adsorption process is said to be endothermic due to the increase in the percentage of fluoride adsorption as temperature value increases [18].

Table 4: Effect of temperature

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Absorbent (g)</th>
<th>Time (min)</th>
<th>C&lt;sub&gt;i&lt;/sub&gt; (mg/L)</th>
<th>C&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
<th>C&lt;sub&gt;i&lt;/sub&gt; - C&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
<th>% Removal</th>
<th>q&lt;sub&gt;e&lt;/sub&gt; (mg/L)</th>
<th>K&lt;sub&gt;0&lt;/sub&gt; = q&lt;sub&gt;e&lt;/sub&gt;/C&lt;sub&gt;e&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>2.5</td>
<td>50</td>
<td>5</td>
<td>2.478</td>
<td>2.522</td>
<td>50.4</td>
<td>25.22</td>
<td>10.18</td>
</tr>
<tr>
<td>313</td>
<td>2.5</td>
<td>50</td>
<td>5</td>
<td>2.217</td>
<td>2.783</td>
<td>55.7</td>
<td>27.83</td>
<td>12.55</td>
</tr>
<tr>
<td>323</td>
<td>2.5</td>
<td>50</td>
<td>5</td>
<td>1.522</td>
<td>3.478</td>
<td>69.6</td>
<td>43.78</td>
<td>28.76</td>
</tr>
<tr>
<td>333</td>
<td>2.5</td>
<td>50</td>
<td>5</td>
<td>1.347</td>
<td>3.653</td>
<td>73.1</td>
<td>36.53</td>
<td>27.12</td>
</tr>
</tbody>
</table>

Adsorption Isotherms

In this investigation, the Freundlich (Figure 6, equation 4) and Langmuir (Figure 7, equation 3) isotherm were used to describe the equilibrium data. The Langmuir isotherm constant K<sub>0</sub> and q<sub>max</sub> were calculated from the slope and intercept of the plot between C<sub>e</sub>/q<sub>e</sub> and C<sub>e</sub>. The isotherm showed good fit with the experimental data with high correlation coefficient (Table 5).

Freundlich constants K<sub>f</sub> and n were calculated from the slope and intercept of the straight line from the plot of log q<sub>e</sub> versus log C<sub>e</sub>. The magnitude of 1/n gives a measure of favourability of adsorption. High values of 1/n; less than 1 represents a favourable sorption [14]

Table 5: Isotherm adsorption parameters

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>q&lt;sub&gt;max&lt;/sub&gt; and 1/n</th>
<th>K&lt;sub&gt;alt&lt;/sub&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir Isotherm</td>
<td>25</td>
<td>-2.86</td>
<td>0.988</td>
</tr>
<tr>
<td>Freundlich Isotherm</td>
<td>0.362</td>
<td>38.91</td>
<td>0.963</td>
</tr>
</tbody>
</table>

Thermodynamics and Mechanism of Adsorption

Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations [19]
where $K_0$ = equilibrium constant; $q_e$ and $C_e$ take their usual meaning, $T$ = temperature in Kelvin and $R$ = gas constant.

The $\Delta H^\circ$ and $\Delta S^\circ$ values were obtained from the slope and intercept of Van’t Hoff plots and presented in Table 6. The values of $\Delta G^\circ$ are within the range of 1 to 93 kJ/mol indicating the favourability of physisorption [20]. From the results, we could confine our self that physisorption is much more favoured. The positive value of $\Delta H^\circ$ confirms the endothermic nature of adsorption and it governs the possibility of physical adsorption. [19]. The value of $\Delta S^\circ$ is positive indicating that the adsorption of fluoride by the ARHA is a spontaneous process [21].

### Table 6: Thermodynamic parameters of fluoride adsorption on ARHA

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_0$</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>1/$T$ (K$^{-1}$)</th>
<th>Log $K_0$</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>10.18</td>
<td>5.84</td>
<td>0.0033</td>
<td>1.008</td>
<td>3.17</td>
<td>1.433</td>
</tr>
<tr>
<td>313</td>
<td>12.55</td>
<td>6.58</td>
<td>0.0032</td>
<td>1.099</td>
<td>3.21</td>
<td>1.459</td>
</tr>
<tr>
<td>323</td>
<td>28.76</td>
<td>9.02</td>
<td>0.0031</td>
<td>1.459</td>
<td>3.25</td>
<td>1.473</td>
</tr>
<tr>
<td>333</td>
<td>27.12</td>
<td>9.14</td>
<td>0.0030</td>
<td>1.433</td>
<td>3.24</td>
<td>1.433</td>
</tr>
</tbody>
</table>

The $\Delta H^\circ$ and $\Delta S^\circ$ using the Van’t Hoff equation

### Table 7: Kinetic parameters of the adsorption of fluoride on ARHA

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Pseudo-first Order</th>
<th>Pseudo-Second-Order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$</td>
<td>$q_e$</td>
</tr>
<tr>
<td>Activated Rice husk (ARHA)</td>
<td>6.656</td>
<td>0.867</td>
</tr>
</tbody>
</table>

The thermodynamic and kinetic parameters of the adsorption or removal of fluoride on activated rice husk ash (ARHA) was determined. The results showed dechlorination by ARHA was favourable, and physisorption mechanism was proposed for the adsorption process. The kinetic parameters showed that the most favourable order for the adsorption process is the pseudo second order reaction. The highest percentage of fluoride removal by ARHA is 86.1 at an exposure time of 60 minutes, which can be said to be very effective in fluoride removal.

### CONCLUSION

The thermodynamic and kinetic parameters of the adsorption or removal of fluoride on activated rice husk ash (ARHA) was determined. The results showed dechlorination by ARHA was favourable, and physisorption mechanism was proposed for the adsorption process. The kinetic parameters showed that the most favourable order for the adsorption process is the pseudo second order reaction. The highest percentage of fluoride removal by ARHA is 86.1 at an exposure time of 60 minutes, which can be said to be very effective in fluoride removal.

### Acknowledgments

We wish to acknowledge the Gombe State University, for furnishing us with the laboratory space, and the chemical reagents used for this research. We also wish to acknowledge the help provided by the laboratory staff of the Department of Chemistry, Gombe State University during the process of the research by helping with setting up some of the equipments used.

### REFERENCE

